

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: C08J 5/18, B32B 27/30, 27/16, C08L 51/00	A1	(11) International Publication Number: WO 98/05706 (43) International Publication Date: 12 February 1998 (12.02.98)
(21) International Application Number: PCT/US97/13551 (22) International Filing Date: 31 July 1997 (31.07.97) (30) Priority Data: 60/022,970 2 August 1996 (02.08.96) US (71) Applicant (for all designated States except US): W.R. GRACE & CO.-CONN. [US/US]; Grace Plaza, 1114 Avenue of the Americas, New York, NY 10036-7794 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): BEKELE, Solomon [US/US]; 4 Walden Way, Taylors, SC 29687 (US). (74) Agents: HURLEY, Rupert, B., Jr. et al.; 100 Rogers Bridge Road, P.O. Box 464, Duncan, SC 29334 (US).		(81) Designated States: AU, BR, CA, CN, JP, KP, KR, MX, NZ, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: FILM HAVING GRAFTED FATTY AMIDE IN OUTERFILM LAYER (57) Abstract A film has an outer surface of a vinyl polymer having a grafted fatty amide. The grafted fatty amide does not migrate within the film. The fatty amide is present on the surface of the film immediately after the formation of the film, and does not have to bloom to the surface of the film to be effective as a slip agent. The fatty amide can be grafted to the polymer by the addition of the fatty amide, and a peroxide, to the extruder, with the heat and pressure within the extruder providing an environment for the grafting reaction to the molten polymer being extruded.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

FILM HAVING GRAFTED FATTY AMIDE IN OUTER FILM LAYER

Field of the Invention

5 The present invention relates generally to films, including both monolayer films and multilayer films, especially packaging films. The present invention also relates to packaged products comprising a product packaged in a film. The present invention is particularly related to films having a relatively low film-to-film and film-to-metal coefficient of friction.

Background of the Invention

10 For some time it has been known to blend a slip agent with a polymer for subsequent extrusion for the formation of a film layer, in order to provide the film with a desired low film-to-film coefficient of friction and film-to-metal coefficient of friction. Regardless of whether the slip agent is added to an inner film layer or an outer film layer, the slip agent tends to bloom to the surface of an outer film layer and thereby provide the film with a lower
15 coefficient of friction, i.e., including both lower film-to-film and film-to-metal coefficients of friction. Even if the slip agent is added to an inner film layer, the slip agent may migrate (i.e., "bloom") to one or more outer surface(s) of the film, thereby becoming effective in decreasing the coefficient of friction.

Summary of the Invention

20 As a first aspect, the present invention is directed to a film having an outer layer comprising a vinyl polymer having grafted fatty amide thereon. Preferably, the grafted fatty amide comprises at least one member selected from the group consisting of grafted primary fatty amide, grafted secondary fatty amide, and grafted tertiary fatty amide; more
25 preferably, at least one member selected from the group consisting of grafted erucamide, grafted oleamide, grafted linoleamide, and grafted linolenamide; still more preferably, at least one member selected from the group consisting of grafted erucamide and grafted oleamide.

30 The film can be a monolayer film or a multilayer film. Preferably, the film is a multilayer film.

One preferred film in accordance with the present invention is a heat-shrinkable film comprising: (a) a first outer layer which serves as a seal layer; (b) a first inner layer comprising an ethylene/alpha-olefin copolymer having a density of from about 0.89 to 0.915; (c) a second inner layer comprising at least one member selected from the group consisting of polyvinylidene chloride, ethylene/vinyl alcohol copolymer, polyamide, polyester, polyethylene carbonate, and polyacrylonitrile; (d) a third inner layer comprising an ethylene/alpha-olefin copolymer having a density of from about 0.89 to 0.915; and (e) a second outer layer which serves as an abuse layer.

The first inner layer is between the first outer layer and the second inner layer, and the second inner layer is between the first inner layer and the third inner layer.

Another preferred multilayer film comprises: outer layers comprising ethylene/vinyl acetate copolymer, an inner layer comprising polyvinylidene chloride, and an inner layer comprising linear low density polyethylene (preferably a blend of 85 weight percent linear low density polyethylene and 15 weight percent ethylene/vinyl acetate copolymer).

Another preferred multilayer film is a biaxially-oriented, heat-shrinkable film comprising:

(a) a first layer, the first layer being an outer layer, the first layer comprising an ethylene/alpha-olefin copolymer having a major differential scanning calorimetry peak of less than 105°C; (b) a second layer, the second layer being an inner O₂-barrier layer; and (c) a third layer, the third layer being a second outer layer, the third layer comprising at least one member selected from the group consisting of ionomer, homogeneous ethylene/alpha-olefin copolymer, ethylene/acrylic acid copolymer, ethylene/methyl acrylic acid copolymer, ethylene/vinyl acetate copolymer, and propylene/ethylene copolymer having an ethylene content of at least 10 percent. The multilayer film has a free shrink, at 185°F, of at least 80 percent, and all layers of the multilayer film are shrink-compatible with respect to one another.

Another preferred multilayer film comprises a first layer having been subjected to an energetic radiation surface treatment in a dosage of up to about 12 MR, said first layer comprising polyamide. Preferably, the first layer serves as a food-contact and food-adhesion layer.

Another multilayer film has low oxygen permeability and comprises: (a) first and second layers, at least one of which comprises an olefin polymer crosslinked from exposure irradiation at a level of from about 2 to 12 MR; and, (b) a third layer which is between the first and second layers, the third layer comprising hydrolyzed ethylene/vinyl acetate copolymer, the multilayer film having a level of heat shrinkage, at 195°F, of at least 10 percent in a longitudinal direction and at least 10 percent in a transverse direction.

Another multilayer film is a hot-blown film comprising: (a) a first layer, the first layer being an outer layer, the first layer comprising at least one member selected from the group consisting of linear low density polyethylene and very low density polyethylene; (b) a second layer, the second layer being an inner layer, the second layer containing a polymer of high molecular weight and fractional melt index which comprises at least one member selected from the group consisting of high density polyethylene, low density polyethylene, and ethylene/vinyl acetate copolymer; (c) a third layer, the third layer being a second inner layer, the third layer comprising polyamide; (d) a fourth layer, the fourth layer being a second outer layer, the fourth layer comprising a self-weldable polymeric material comprising at least one member selected from the group consisting of copolyamide and ethylene/vinyl acetate copolymer; (e) a fifth layer comprising a chemically modified ethylene unsaturated ester copolymer; and (f) a sixth layer which is an O₂-barrier layer comprising at least one member selected from the group consisting of ethylene/vinyl alcohol copolymer, vinylidene chloride copolymer, and polyamide. The second layer is adjacent the first layer and the fifth layer is between the second layer and the third layer and third layers.

Another preferred multilayer film is a hot-blown film comprising: (a) a first layer, the first layer being an outer layer, the first layer comprising at least one member selected from the group consisting of ethylene/alpha-olefin copolymer, fractional melt index low density polyethylene, and ethylene/ester copolymer; (b) a second layer which is adhered to the first layer, the second layer being an inner layer, the second layer containing an abuse-resistant polymer comprising at least one member selected from the group consisting of very low density polyethylene, ethylene/vinyl acetate copolymer having a fractional melt index, and ionomer; (c) a third layer, the third layer being a second inner layer, the third layer comprising chemically-modified polyolefinic adhesive; (d) a fourth layer, the fourth

layer being a third inner layer, the fourth layer comprising at least one member selected from the group consisting of polyamide 6 and copolyamide; (e) a fifth layer adhered to the fourth layer, the fifth layer comprising ethylene/vinyl alcohol copolymer; (f) a sixth layer adhered to the fifth layer, the sixth layer comprising at least one member selected from the group consisting of polyamide 6, copolyamide, and nucleated polyamide 6; and (g) a seventh layer adhered to the sixth layer, the seventh layer comprising a self-weldable chemically modified polyolefinic adhesive. The third layer is between the second layer and the fourth layer and wherein the film is present as a lay-flat tubing and wherein the seventh layer is bonded to itself.

10 Another preferred multilayer film comprises: (a) a first layer comprising a first homogeneous ethylene/alpha-olefin copolymer; (b) a second layer comprising polyolefin; and (c) a third layer comprising a second homogeneous ethylene/alpha-olefin copolymer. The second layer is between the first layer and the third layer, the second layer is chemically different from the first layer and the third layer, and the multilayer film has an oxygen
15 transmission rate of from about 500 to 50,000 cc/m² 24hr STP.

Another preferred multilayer film comprises: (a) a first outer layer comprising: (i) a polymeric component comprising at least one member selected from the group consisting of ethylene homopolymer, ethylene/alpha-olefin copolymer, ethylene/ester copolymer, ethylene/acid copolymer, and ionomer; and (ii) a surface-active agent component comprising
20 at least one member selected from the group consisting of ester of aliphatic alcohol, polyether, polyhydric alcohol, ester of polyhydric aliphatic alcohol, and polyethoxylated aromatic alcohol; (b) at least one inner layer comprising polyolefin; and (c) a second outer layer comprising at least one member selected from the group consisting of ethylene homopolymer, ethylene/alpha-olefin copolymer, ethylene/ester copolymer, ethylene/acid
25 copolymer, and ionomer. The surface-active component is present over the entire outside surface of the first outer layer, the inner layer is between the first outer layer and the second outer layer, the inner layer is chemically different from the first outer layer and the second outer layer, and the multilayer film has an O₂-transmission rate of from about 500 to 50,000 cc/m² 24hr STP.

30 Another preferred multilayer film comprises (a) a first outer layer comprising a first ethylene/alpha-olefin copolymer, wherein the first ethylene/alpha-olefin copolymer comprises

homogeneous copolymer; (b) an inner layer comprising a thermoplastic elastomer; and (c) a second outer layer comprising a second ethylene/alpha-olefin copolymer. The inner layer is between the first outer layer and the second outer layer, the inner layer is chemically different from the first outer layer and the second outer layer, and the multilayer film has an O₂-transmission rate of from about 500 to 50,000 cc/m² 24hr STP, and the multilayer film has a modulus of from about 60,000 to 150,000 psi.

Another preferred multilayer film is a thermoformable film comprising: (a) a first layer which is a core layer which comprises an O₂-barrier composition; (b) a second layer and a third layer, each of which is directly adhered to a surface of the first layer, each of the second layer and the third layer comprising polyamide and a nucleating agent; (c) a fourth layer which is a first outer layer and which serves as a sealing layer; and (d) a fifth layer which is a second outer layer and which comprises a moisture barrier composition.

Another preferred multilayer film is a coextruded, tubular, and laminated, and is suitable for use in elevated temperature media, comprising: (a) a first layer comprising a film-forming polyamide; (b) a second layer comprising an alpha-olefin polymer or copolymer; and, (c) an adhesive between the first and second layers, the adhesive comprising alpha-olefin mer units as a major component thereof. The adhesive and the alpha-olefin polymer or copolymer are each crosslinked by irradiation at a dosage level of at least about 6 MR.

Another preferred multilayer film is an oriented, heat-shrinkable film comprising: (a) a first layer which is a cross-linked inner layer comprising a blend comprising ethylene/vinyl alcohol copolymer and polyamide, the first layer having a thickness of from about 5 to 25 percent of a total thickness of the multilayer film; (b) a second layer and a third layer, each of which is an inner film layer, each of which comprises a crosslinked polymer, and each of which comprises an adhesive resin; (c) a fourth layer and a fifth layer, each of which is an outer film layer, each of which comprises a three-component blend of linear low density polyethylene, linear medium density polyethylene, and ethylene/vinyl acetate copolymer. The total thickness of the multilayer film is from about 0.75 to 1.5 mils.

Another preferred multilayer film is an oriented, heat-sealable film comprising: (a) first and second layers each of which are outer layers comprising a blend comprising linear

low density polyethylene, linear medium density polyethylene, and, ethylene/vinyl acetate copolymer; and (b) a third layer which is an inner layer comprising a crosslinked polymer consisting essentially of linear low density polyethylene.

Another preferred multilayer film is an oriented film comprising: (a) first and
5 second layers each of which is an outer layer comprising linear low density polyethylene, linear medium density polyethylene, and, ethylene/vinyl acetate copolymer; and (b) a third layer which is an inner layer comprising a member selected from the group consisting of (i) ethylene/vinyl acetate copolymer; and (ii) in combination, linear low density polyethylene, linear medium density polyethylene, and ethylene/vinyl acetate; and, (c)
10 fourth and fifth layers each of which is an inner layer comprising linear low density polyethylene; and wherein the third layer is between the fourth and fifth layers.

Another preferred multilayer film is a heat-shrinkable film comprising: (a) first and second layers each of which is an outer layer; and (b) a third layer which is an inner layer comprising a member selected from the group consisting of (i) ethylene homopolymer,
15 ethylene copolymer, and ethylene terpolymer, and (ii) a blend of ethylene homopolymer or ethylene copolymer with butylene homopolymer or butylene copolymer. At least one layer of the multilayer film is stretch-oriented and comprises at least one member selected from the group consisting of polyester and copolyester.

Another preferred multilayer film is a heat-shrinkable comprising: (a) first and
20 second layers each of which is an outer layer; and (b) a third layer which is an inner layer comprising from 70 to 90 weight percent, based on layer weight, of at least one member selected from the group consisting of ethylene homopolymer and ethylene copolymer, butylene homopolymer, and butylene copolymer, wherein from about 10 to 30 weight percent of the third layer is selected from the group consisting of butylene homopolymer and butylene copolymer. At least one film layer comprises at least one member selected
25 from the group consisting of propylene homopolymer and propylene copolymer.

Another preferred multilayer film comprises: (a) first and second layers each of which is an outer layer comprising ethylene propylene copolymer in an amount of from about 70 to 90 weight percent, based on layer weight, and propylene homopolymer in an
30 amount of from about 10 to 30 weight percent, based on layer weight; and (b) a third layer which is an inner layer comprising at least one member selected from the group

consisting of linear low density polyethylene and linear medium density polyethylene. The multilayer film has an average machine direction free shrink at 200°F of at least 12% and an average transverse direction free shrink at 200°F of at least about 17%.

Another preferred multilayer film comprises: (a) a first layer consisting essentially
5 of a crosslinked ethylene/vinyl acetate copolymer; (b) a second layer comprising an O₂-barrier material comprising vinyl chloride-vinylidene chloride copolymer; and (c) a third layer comprising a non-crosslinked ethylene/vinyl acetate copolymer.

Another preferred multilayer film comprises: (a) an inner layer comprising homogeneous ethylene/alpha-olefin copolymer having a density of from about 0.89 to
10 0.92 grams per cubic centimeter; (b) a first outer layer comprising at least one member selected from the group consisting of propylene homopolymer, propylene copolymer, a blend of homopolymer or copolymer of polypropylene and elastomer, high density polyethylene, and copolyester; and (c) a second outer layer comprising at least one member selected from the group consisting of polyamide, copolyamide, polyester,
15 copolyester, high density polyethylene, polypropylene, propylene/ethylene copolymer, and polycarbonate.

Another preferred multilayer film comprises: (a) a first layer comprising a blend of elastomer and at least one member selected from the group consisting of propylene homopolymer and propylene copolymer; and (b) a second layer in adherence with the first
20 layer, the second layer comprising an ethylene/alpha-olefin copolymer having a density of less than or equal to 0.89 grams per cubic centimeter.

Another preferred multilayer film comprises: (a) a first layer comprising at least one member selected from the group consisting of ethylene/vinyl acetate copolymer and linear low density polyethylene, wherein the first layer is an inner layer; (b) second and
25 third layers directly adhered to the first layer, both the second layer and the third layer being inner layers, and both the second and third layers consisting essentially of a linear low density polyethylene; and (c) fourth and fifth layers, each of which is an outer film layer, each of which consists essentially of ethylene/vinyl acetate copolymer. The multilayer film has a shrink tension, at 205°F, of at least about 450 psi in a transverse
30 direction, and at least about 450 psi in a longitudinal direction, and wherein the multilayer

film has an elongation to break, at 73°F, of at least about 200% in the transverse direction and at least about 200% in the longitudinal direction.

Another preferred multilayer film is a coextruded film comprising: (a) a first layer which is an inner layer comprising ethylene/vinyl alcohol copolymer; (b) a second layer and a third layer, each of which are inner layers comprising polyamide; (c) a fourth layer and a fifth layer, each of which are inner layers comprising an adhesive polymer; and (d) a sixth layer and a seventh layer, each of which are outer layers comprising a blend of linear low density polyethylene and an anti-blocking agent, the linear low density polyethylene being present in an amount of from about 85 to 99 percent, based on layer weight, and the anti-blocking agent being present in an amount of from about 1 to 15 percent, based on layer weight. The first layer is between the second layer and the third layer, and the first, second, and third layers are between the fourth layer and the fifth layer.

Another preferred multilayer film comprises: (a) a first layer and a second layer, both of which are outer layers containing a polymer comprising at least one member selected from the group consisting of: (i) olefin, and (ii) polyester; and (b) a third layer which is an inner layer and which comprises polyolefin. The third layer is between the first layer and the second layer and the film has a maximum average machine direction shrink tension of no more than about 300 psi, and a maximum average transverse direction shrink tension of no more than about 300 psi, said shrink tension values being measured under ASTM D 2838, and the polymer in the first and second layers comprises polymer having a melting point at least about 10°C higher than a melting point of the polyolefin in the third layer.

Another preferred multilayer film comprises: (a) a first layer and a second layer, both of which are outer layers containing a polymer comprising at least one member selected from the group consisting of linear low density polyethylene, and ethylene/propylene copolymer; (b) a third layer which is an inner layer and which comprises at least one member selected from the group consisting of linear low density polyethylene, and ethylene/propylene copolymer; and (c) a fourth layer and a fifth layer, each of which comprises a polymer having a melting point of less than about 100°C. The film has an average machine direction shrink tension at 205°F of no more than about 250

psi, and an average transverse direction shrink tension at 205°F of no more than about 300 psi, said shrink tension values being measured under ASTM D 2838.

Another preferred multilayer film is a gas permeable film which can be manually delaminated from a gas impermeable film, wherein: (a) the gas-permeable film comprises:

5 (i) a first layer which serves as a heat-sealable layer and which comprises at least one member selected from the group consisting of ethylene homopolymer and ethylene copolymer; and (ii) a second layer which comprises linear ethylene/alpha-olefin copolymer having a density of less than about 0.915 g/cc. The gas-impermeable film comprises: (i) a

10 first layer which comprises at least one member selected from the group consisting of ethylene/vinyl alcohol copolymer, vinylidene chloride copolymer, and vinylidene chloride terpolymer, this first layer being directly to the second layer of the gas-permeable film in a manner so that when delamination occurs the barrier layer becomes a first surface layer; and (ii) a second layer comprising a polymer, the second layer being an outer layer. The first layer of the gas-permeable film is capable of sealing to a polymeric surface with a

15 bond strength greater than a force required to rupture and subsequently delaminate the gas-permeable film from the gas-impermeable film.

Another preferred multilayer film is a film which is suitable for use in vacuum skin packaging, comprising: (a) a first layer which is a bonding layer comprising at least one member selected from the group consisting of low density polyethylene, high density

20 polyethylene, and ionomer; (b) a second layer which is a complementary layer comprising an ethylene/vinyl acetate copolymer comprising vinyl acetate mer in an amount of from about 15 to 25 percent, based on copolymer weight, the remainder of the copolymer comprising ethylene mer, wherein the copolymer is crosslinked, the second layer having a thickness of from about 16 to 225 microns; and (c) a third layer which is an outer layer

25 which is coextruded with the first layer, the second layer being between the first layer and the third layer, the third layer comprising at least one member selected from the group consisting of low density polyethylene, high density polyethylene, linear low density polyethylene, ionomer, and ethylene vinyl acetate copolymer having a vinyl acetate content of from about 3 to 9 percent, based on copolymer weight.

30 Another preferred multilayer film is a high O₂-barrier implosion-resistant film comprising: (a) a first layer which is an inner layer comprising ethylene/vinyl alcohol

copolymer; (b) a second layer and a third layer, each of which is an inner layer which serves as a tie layer; (c) a fourth layer and a fifth layer, each of which is an inner layer comprising ethylene/vinyl acetate copolymer; (d) a sixth layer, which is an outer layer and which comprises a heat-sealable polymer; (e) a seventh layer, which is an outer layer, and
5 which comprises a heat-resistant polymer; and (f) an eighth layer and a ninth layer, each of which is an inner layer which serves as a moisture-resistant layer, the eighth layer being between the fourth layer and the sixth layer, and the ninth layer being between the fifth layer and the seventh layer.

Another preferred multilayer film is a heat-shrinkable film comprising a
10 homogeneous single-site catalyzed copolymer of ethylene and an alpha-olefin having from three to ten carbon atoms, said copolymer having a density of at least about 0.90 g/cc, wherein the film has an outer surface comprising a vinyl polymer having grafted fatty amide thereon.

Another preferred multilayer film is a heat-shrinkable and has a substantially
15 symmetrical structure comprising: (a) outer layers comprising at least one member selected from the group consisting of propylene homopolymer and propylene copolymer; and (b) an inner layer comprising a homogeneous single-site-catalyzed copolymer of ethylene and an alpha-olefin having from four to eight carbon atoms.

Another preferred multilayer film is a heat-shrinkable film comprising: (a) a first
20 layer which is an outer layer and which serves as a heat sealing layer; (b) a second layer which is an inner layer and which comprises a homogeneous single-site-catalyzed copolymer of ethylene and an alpha-olefin having from three to ten carbon atoms, the copolymer having a density of at least about 0.90 g/cc; and (c) a third layer which is an O₂-barrier layer.

25 Another preferred multilayer film is a heat-shrinkable film comprising: (a) a first layer which is an outer layer and which serves as a heat sealing layer comprising a homogeneous single-site-catalyzed copolymer of ethylene and an alpha-olefin having from three to eight carbon atoms, the copolymer having a density of at least about 0.90 g/cc; and (b) a second layer which is an O₂-barrier layer.

30 Another preferred multilayer film is a heat-shrinkable film comprising at least one layer comprising a homogeneous single-site-catalyzed copolymer of ethylene and an

alpha-olefin having from three to eight carbon atoms, the copolymer having a density of at least about 0.90 g/cc, wherein at least one layer of the film comprises a crosslinked polymer network.

Another preferred multilayer film is a heat-shrinkable film having a substantially
5 symmetrical structure and comprising: (a) first and second outer layers comprising a homogeneous single-site-catalyzed copolymer of ethylene and an alpha-olefin having from three to eight carbon atoms, the copolymer having a density of at least about 0.90 g/cc, (B) a third layer which is an inner layer.

Another preferred film is a heat-shrinkable film having an impact strength of at
10 least 35 pounds, per mil of homogeneous polymer. More preferably, the film has an impact strength of from about 35 to 90 pounds, per mil of homogeneous polymer; still more preferably, from about 35 to 65 pounds, per mil of homogeneous polymer; yet still more preferably, from about 60 to 90 pounds, per mil of homogeneous polymer. Preferably, the film is a multilayer film, and the homogeneous polymer is present in a core
15 layer. Preferably, the homogeneous polymer is present in a film layer in an amount of about 100 percent, based on the weight of the film layer, the film layer having a thickness of about 1 mil. Preferably, the multilayer film further comprises an outer sealant layer and a barrier layer. Preferably, the multilayer film further comprises an outer abuse layer. Preferably, the multilayer film further comprises at least one tie layer; more preferably, the
20 multilayer film comprises a first tie layer between the barrier layer and the outer sealant layer, and a second tie layer between the barrier layer and the abuse layer. Alternatively, the film is a monolayer film having an impact strength at least 35 pounds, per mil of homogeneous polymer.

Preferably, the film is a heat-shrinkable film comprising homogeneous ethylene/alpha-
25 olefin copolymer, the film having an impact strength of from about 35 to 200 pounds and a total free shrink, at 185°F, of from about 80 to 150 percent; more preferably, the film has an impact strength of from about 40 to 90 pounds; still more preferably, the heat-shrinkable film has a total free shrink at 185°F, of from about 80 to 120 percent. Preferably, the heat-shrinkable film has a total thickness of from about 1 to 3 mils.

30 Another preferred film is a monolayer or multilayer film comprising homogeneous ethylene/alpha-olefin copolymer, more preferably in an inner layer of a multilayer film.

Preferably, the homogeneous ethylene/alpha-olefin copolymer is present in the inner layer in an amount of from about 60 to 100 weight percent, based on the weight of the inner layer, and wherein the inner layer has a thickness of about 1 to 3 mils; more preferably, the homogeneous ethylene/alpha olefin copolymer is present in the inner layer in an amount of about 80 to 100 weight percent, based on the weight of the inner layer, and wherein the inner layer has a thickness of about 1 to 2.5 mils; more preferably, the homogeneous ethylene/alpha olefin copolymer is present in the inner layer in an amount of about 90 to 100 weight percent, based on the weight of the inner layer.

In another preferred film, the homogeneous ethylene/alpha olefin copolymer is a first component present in a composition which further comprises a second component comprising least one member selected from the group consisting of another ethylene/alpha-olefin copolymer, ethylene/vinyl acetate copolymer, ethylene/vinyl ester copolymer, ethylene/acrylic acid copolymer, propylene/ethylene copolymer, polyethylene homopolymer, polypropylene homopolymer, and ionomer, wherein the second component is present in the composition in an amount of from about 1 to 40 weight percent, based on the weight of the composition. Preferably, the first component and the second component are in a substantially uniform blend. Preferably, the homogeneous ethylene/alpha olefin copolymer is present in a composition which further comprises at least one member selected from the group consisting of a maleic anhydride grafted ethylene/alpha-olefin copolymer, maleic anhydride grafted ethylene/vinyl acetate copolymer, maleic anhydride grafted ethylene/vinyl ester copolymer, maleic anhydride grafted ethylene/acrylic acid copolymer, maleic anhydride grafted propylene/ethylene copolymer, maleic anhydride grafted polyethylene homopolymer, maleic anhydride grafted polypropylene homopolymer, and maleic anhydride grafted ionomer.

Another preferred heat-shrinkable multilayer film comprises an O₂-barrier layer and an outer sealant layer. Preferably, the outer sealant layer is a first outer layer, and an outer abuse layer is a second outer layer. Preferably, the heat-shrinkable film further comprises at least one tie layer between the barrier layer and the first outer layer. Preferably, the tie layer between the barrier layer and the first outer layer is a first tie layer, and a second tie layer is between the barrier layer and the second outer layer.

Another preferred film is a multilayer heat-shrinkable film, with a film layer comprising the homogeneous ethylene/alpha-olefin copolymer being a first outer film layer. Preferably, the homogeneous ethylene/alpha-olefin copolymer in the first outer film layer is a first homogeneous ethylene/alpha-olefin copolymer, the film further comprising
5 a second outer film layer comprising a second homogeneous ethylene/alpha-olefin copolymer. Preferably, the first homogeneous ethylene/alpha-olefin copolymer is substantially identical to the second homogeneous ethylene/alpha-olefin copolymer. Preferably, the first and second outer layers are substantially identical in chemical composition and thickness, and the heat-shrinkable film is substantially symmetrical.

10 Another preferred multilayer film is a heat-shrinkable film comprising: a first inner layer, a second inner layer, and a third inner layer, wherein the first inner layer is a first tie layer, the second inner layer is an O₂-barrier layer, and the third inner layer is a second tie layer, the first and second outer layers are substantially identical in chemical composition and thickness, the first and second tie layers are substantially identical in chemical
15 composition and thickness, with the heat-shrinkable film being substantially symmetrical.

Another preferred multilayer film is a heat-shrinkable film comprising homogeneous ethylene/alpha-olefin copolymer, the heat-shrinkable film having an impact strength of from about 80 to 250 pounds and a total free shrink, at 185°F, of from about 30 to 150 percent. Preferably, the heat-shrinkable film has an impact strength of from
20 about 80 to 200 pounds, and a total free shrink, at 185°F, of from about 50 to 120 percent. The heat-shrinkable film is a monolayer film or a multilayer film. Preferably, the heat-shrinkable film is a multilayer heat-shrinkable film, and the layer comprising the homogeneous ethylene/alpha olefin copolymer is an inner layer.

Another preferred multilayer film comprises a homogeneous single site catalyzed
25 copolymer of ethylene and an alpha-olefin having from three to ten carbon atoms, wherein the single site catalyzed copolymer has long chain branching.

Another preferred multilayer film comprises a homogeneous single site catalyzed copolymer of ethylene and an alpha-olefin having from three to ten carbon atoms, said single site catalyzed copolymer having limited long chain branching.

30 Another preferred multilayer film is a heat-shrinkable film comprising a single-site-catalyzed ethylene/alpha olefin copolymer wherein the alpha-olefin has from four to eight

carbon atoms. Preferably, the single-site-catalyzed copolymer is blended with another thermoplastic homopolymer or copolymer. Preferably, the single site catalyzed copolymer has a density of from about 0.86 to 0.95 g/cc. Preferably, the film is a multilayer film.

5 Another preferred multilayer film is a heat-shrinkable film comprising at least one inner core layer comprising a homogeneous single site catalyzed copolymer of ethylene and an alpha-olefin having from four to ten carbon atoms and having at least some long chain branching (i.e., a substantially linear ethylene/alpha-olefin copolymer having long chain branching), the copolymer having a density of from about 0.89 g/cc to about 0.91
10 g/cc.

Another preferred multilayer film is a heat-shrinkable film comprising the general structure: seal/core/barrier/core/abuse, wherein each of the core layers comprises the same homogeneous long chain branched single-site catalyzed copolymer of ethylene and an alpha-olefin having from four to ten carbon atoms, said copolymer having a density of from about
15 0.89 g/cc to about 0.91 g/cc.

Another preferred multilayer film is a heat-shrinkable film comprising: (a) a seal layer; (b) a first inner layer comprising a homogeneous, long chain branched ethylene/alpha-olefin copolymer having a density of from about 0.89 to 0.91 g/cc; (c) an O₂-barrier layer; (d) a second inner layer comprising a homogeneous, long chain branched ethylene/alpha-olefin
20 copolymer having a density of from about 0.89 to 0.91 g/cc; and (e) an abuse layer, wherein the homogeneous, long chain branched ethylene/alpha-olefin copolymer in the first inner layer differs from the homogeneous, long chain branched ethylene/alpha-olefin copolymer in the second inner layer.

Another preferred multilayer film is a heat-shrinkable film comprising: (a) a sealing
25 layer comprising a homogeneous, single-site-catalyzed copolymer of ethylene and an alpha-olefin having from four to ten carbon atoms, the copolymer having long chain branching and a density of from about 0.89 g/cc to about 0.91 g/cc; (b) an O₂-barrier layer; (c) an abuse layer comprising a second inner layer comprising a homogeneous, long chain branched ethylene/alpha-olefin copolymer having a density of from about 0.89 to 0.91 g/cc;
30 and (d) an abuse layer comprising a homogeneous, single-site-catalyzed copolymer of

ethylene and an alpha-olefin having from four to ten carbon atoms, the copolymer having long chain branching and a density of from about 0.89 g/cc to about 0.91 g/cc.

Another preferred multilayer film is a heat-shrinkable film comprising the general structure: seal/core/barrier/core/abuse, wherein each of the two core layers comprises the same
5 homogeneous copolymer of ethylene and octene having an I_{10}/I_2 greater than or equal to 5.63 and a M_w/M_n less than or equal to $(I_{10}/I_2) - 4.63$, said copolymer having a density of from about 0.89 g/cc to about 0.91 g/cc.

Another preferred multilayer film is a heat-shrinkable film comprising: (a) a sealing layer; (b) a first inner layer comprising a homogeneous ethylene octene copolymer having an
10 I_{10}/I_2 greater than or equal to 5.63 and a M_w/M_n less than or equal to $(I_{10}/I_2) - 4.63$, said copolymer having a density of from about 0.89 g/cc to about 0.91 g/cc; (c) an O_2 -barrier layer; (d) a second inner layer comprising a homogeneous ethylene octene copolymer having an I_{10}/I_2 greater than or equal to 5.63 and a M_w/M_n less than or equal to $(I_{10}/I_2) - 4.63$, said copolymer having a density of from about 0.89 g/cc to about 0.91 g/cc; and (E) an abuse layer.

15 Another preferred multilayer film is a heat-shrinkable film comprising the general structure: seal/core/abuse wherein the core layer comprises a homogeneous long chain branched single site catalyzed copolymer of ethylene and an alpha-olefin having from four to ten carbon atoms, said copolymer having a density of from about 0.89 g/cc to about 0.91 g/cc.

In the film of the present invention, preferably the fatty acid amide is present in the
20 outer layer in an amount of from about 0.005 to 5 weight percent, based on the weight of the outer layer; more preferably, the fatty acid amide is present in the outer layer in an amount of from about 0.025 to 3 weight percent, based on the weight of the outer layer; still more preferably, from about 0.05 to 0.45 weight percent, based on the weight of the outer layer.

25 As a second aspect, the present invention is directed to an article comprising a heat-shrinkable multilayer film comprising a film layer comprising homogeneous ethylene/alpha-olefin copolymer, wherein the heat-shrinkable film has an impact strength of from about 35 to 200 pounds and a total free shrink, at 185°F, of from about 80 to 150 percent, and wherein the article is a member selected from the group consisting of a bag and a casing,
30 and wherein the film has an outer layer comprising a vinyl polymer having a grafted fatty amide thereon.

As a third aspect, the present invention is directed to a method of making a grafted polymer. The method comprises mixing a vinyl polymer with a peroxyketal initiator and an unsaturated fatty amide; and reacting the vinyl polymer with the unsaturated fatty amide in the presence of a peroxyketal initiator, wherein the reacting is carried out in a batch reactor comprising an intensive internal mixer that is capable of generating high shear to achieve a homogeneous melt, so that a vinyl polymer having a grafted fatty amide is produced. Preferably, the intensive internal mixer comprises at least one member selected from the group consisting of a cam mixer, a sigma mixer, a roller mixer, a banbury mixer, a corotating twin screw extruder, and a single screw extruder. Preferably, the fatty amide is present at a concentration of from about 250 ppm to 5000 ppm.

As a fourth aspect, the present invention is directed to a method of making a film having an outer surface comprising grafted fatty amide, comprising: (A) preparing a vinyl polymer having a grafted fatty amide thereon, by: (i) mixing a vinyl polymer with a peroxyketal initiator and an unsaturated fatty amide; and (ii) reacting the vinyl polymer with the unsaturated fatty amide in the presence of the peroxyketal initiator. The reacting is carried out in a batch reactor comprising a mixer that is capable of generating high shear to achieve a homogeneous melt, so that a vinyl polymer having a grafted fatty amide is produced; (B) extruding the vinyl polymer having grafted fatty amide to form a film, wherein the extrusion is carried out so that the vinyl polymer having the grafted fatty amide is present on an outer film surface. Preferably, the mixer comprises at least one member selected from the group consisting of a corotating twin screw extruder and a single screw extruder, and wherein the mixing, reacting, and extruding are carried out sequentially in the same mixer.

25

Detailed Description of the Invention

As used herein, the term "film" is used in a generic sense to include plastic web, regardless of whether it is film or sheet. Preferably, films of and used in the present invention have a thickness of 0.25 mm or less. As used herein, the term "package" refers to packaging materials configured around a product being packaged. The phrase "packaged product," as

30

used herein, refers to the combination of a product which is surrounded by a packaging material.

As used herein, the term "seal" refers to any seal of a first region of a film surface to a second region of a film surface, wherein the seal is formed by heating the regions to at least their respective seal initiation temperatures. The sealing can be performed by any one or more of a wide variety of manners, such as using a heated bar, hot air, hot wire, infrared radiation, ultrasonic sealing, radio frequency sealing, etc. However, the preferred sealing mechanism is a seal made on a bag machine using a hot-wire.

Although the film preferably has a film-to-film coefficient of friction of from about 0.1 to 0.9, more preferably the film has a film-to-film coefficient of friction of from about 0.1 to 0.7, still more preferably, from about 0.1-0.6, and yet still more preferably, from about 0.1 to 0.5.

Fatty amides useful in the present invention are disclosed in A.L. McKenna, Fatty Amides, c.1982, Witco Chemical Corporation, which is hereby incorporated, in its entirety, by reference thereto.

As used herein, the phrases "food-contact layer" and "meat-contact layer" refer to a layer of a multilayer film which is in direct contact with the food/meat in the package comprising the film. In a multilayer film, a food-contact layer is always an outer film layer, as the food-contact layer is in direct contact with the food product within the package. The food-contact layer is an inside layer in the sense that with respect to the packaged food product, the food-contact layer is the inside layer (i.e., innermost layer) of the package, this inside layer being in direct contact with the food. As used herein, the phrases "food-contact surface" and "meat-contact surface" refer to an outer surface of a food contact layer, this outer surface being in direct contact with the food within the package.

As used herein, the phrase "cook-in" refers to the process of cooking a product packaged in a material capable of withstanding exposure to long and slow cooking conditions while containing the food product, for example submersion in water at 57°C to 121°C (i.e., 135°F-250°F) for 2-12 hours, preferably 57°C to 100°C (i.e., 135°F-250°F) for 2-12 hours. Cook-in packaged foods are essentially pre-packaged, pre-cooked foods which may be directly transferred to the consumer in this form. These types of foods may be consumed with or without warming. Cook-in packaging materials maintain seal integrity, and in the case of

multilayer films are delamination resistant. Cook-in films must also be heat shrinkable under cook-in conditions so as to form a tightly fitting package. Cook-in films preferably have a tendency for adhesion to the food product, thereby preventing "cook-out", which is the collection of juices between the outer surface of the food product and the meat-contact surface of the film, i.e., the surface in direct contact with the meat. Additional optional characteristics of films for use in cook-in applications include delamination-resistance, low O₂-permeability, heat-shrinkability representing about 20-50% biaxial shrinkage at about 85°C (185°F), and optical clarity. For hermetically sealed bags, it is preferred that the external surface of the package is subjected to a temperature of at least about 150°F; preferably from about 150°F to 212°F; more preferably, from about 160 to 212°F; still more preferably, from about 165°F to 200°F; and, even yet still more preferably, from about 170°F to 180°F.

As used herein, the term "barrier", and the phrase "barrier layer", as applied to films and/or film layers, are used with reference to the ability of a film or film layer to serve as a barrier to one or more gases. In the packaging art, oxygen (i.e., gaseous O₂) barrier layers have included, for example, hydrolyzed ethylene/vinyl acetate copolymer (designated by the abbreviations "EVOH" and "HEVA", and also referred to as "ethylene/vinyl alcohol copolymer"), polyvinylidene chloride, polyamide, polyester, polyacrylonitrile, etc., as known to those of skill in the art.

As used herein, the phrase "abuse layer", as well as the phrase "puncture-resistant layer", refer to an outer film layer and/or an inner film layer, so long as the film layer serves to resist abrasion, puncture, and other potential causes of reduction of package integrity, as well as potential causes of reduction of package appearance quality.

As used herein, the terms "lamination," "laminated," as well as the phrase "laminated film," refer to the process, and resulting product, made by bonding together two or more layers of film or other materials. Lamination can be accomplished by joining layers with adhesives, joining with heat and pressure, with corona treatment, and even spread coating and extrusion coating. The term laminate is also inclusive of coextruded multilayer films comprising one or more tie layers.

As used herein, the term "oriented" refers to a polymer-containing material which has been elongated (generally at an elevated temperature called the orientation temperature), followed by being "set" in the elongated configuration by cooling the material while

substantially retaining the elongated dimensions. This combination of elongation at elevated temperature followed by cooling causes an alignment of the polymer chains to a more parallel configuration, thereby improving the mechanical properties of the film. Upon subsequently heating unrestrained, unannealed, oriented polymer-containing material to its orientation temperature, heat shrinkage is produced almost to the original dimensions, i.e., pre-elongation dimensions. The term "oriented," is herein used with reference to oriented films, which can undergo orientation in any one or more of a variety of manners.

Orienting in one direction is referred to herein as "uniaxial orientation," while orienting in two directions is referred to herein as "biaxial orientation." In oriented plastic films, there can be internal stress remaining in the plastic sheet which can be relieved by reheating the film to a temperature above that at which it was oriented. Upon reheating such a film, the film tends to shrink back to the original dimensions it had before it was oriented. Films which shrink upon being heated are generally referred to as heat-shrinkable films.

As used herein, the phrase "orientation ratio" refers to the multiplication product of the extent to which the plastic film material is oriented in several directions, usually two directions perpendicular to one another. Orientation in the machine direction is herein referred to as "drawing", whereas orientation in the transverse direction is herein referred to as "stretching". For films extruded through an annular die, stretching is obtained by "blowing" the film to produce a bubble. For such films, drawing is obtained by passing the film through two sets of powered nip rolls, with the downstream set having a higher surface speed than the upstream set, with the resulting draw ratio being the surface speed of the downstream set of nip rolls divided by the surface speed of the upstream set of nip rolls. The degree of orientation is also referred to as the orientation ratio, also known as the "racking ratio".

As used herein, the term "monomer" refers to a relatively simple compound, usually containing carbon and of low molecular weight, which can react to form a polymer by combining with itself or with other similar molecules or compounds.

As used herein, the term "comonomer" refers to a monomer which is copolymerized with at least one different monomer in a copolymerization reaction, the result of which is a copolymer.

As used herein, the term "polymer" refers to the product of a polymerization reaction, and is inclusive of homopolymers, copolymers, terpolymers, tetrapolymers, etc. In general, the layers of a film can consist essentially of a single polymer, or can have additional polymers together therewith, i.e., blended therewith.

5 As used herein, the term "homopolymer" is used with reference to a polymer resulting from the polymerization of a single monomer, i.e., a polymer consisting essentially of a single type of repeating unit.

As used herein, the term "copolymer" refers to polymers formed by the polymerization reaction of at least two different monomers. For example, the term "copolymer" includes the
10 copolymerization reaction product of ethylene and an alpha-olefin, such as 1-hexene. The term "copolymer" is also inclusive of, for example, the copolymerization of a mixture of ethylene, propylene, 1-hexene, and 1-octene. As used herein, the term "copolymerization" refers to the simultaneous polymerization of two or more monomers. The term "copolymer" is also inclusive of random copolymers, block copolymers, and graft copolymers.

15 As used herein, the term "polymerization" is inclusive of homopolymerizations, copolymerizations, terpolymerizations, etc., and includes all types of copolymerizations such as random, graft, block, etc. In general, the polymers, in the films used in accordance with the present invention, can be prepared in accordance with any suitable polymerization process, including slurry polymerization, gas phase polymerization, and high pressure polymerization
20 processes.

As used herein, a copolymer identified in terms of a plurality of monomers, e.g., "propylene/ethylene copolymer", refers to a copolymer in which either monomer may copolymerize in a higher weight or molar percent than the other monomer or monomers. However, the first listed monomer preferably polymerizes in a higher weight percent than the
25 second listed monomer, and, for copolymers which are terpolymers, quadripolymers, etc., preferably the first monomer copolymerizes in a higher weight percent than the second monomer, and the second monomer copolymerizes in a higher weight percent than the third monomer, etc.

As used herein, terminology employing a "/" with respect to the chemical identity of a
30 copolymer (e.g., "an ethylene/alpha-olefin copolymer"), identifies the comonomers which are

copolymerized to produce the copolymer. As used herein, "ethylene alpha-olefin copolymer" is the equivalent of "ethylene/alpha-olefin copolymer."

As used herein, copolymers are identified, i.e. named, in terms of the monomers from which the copolymers are produced. For example, the phrase "propylene/ethylene copolymer" refers to a copolymer produced by the copolymerization of both propylene and ethylene, with or without additional comonomer(s). As used herein, the phrase "mer" refers to a unit of a polymer, as derived from a monomer used in the polymerization reaction. For example, the phrase "alpha-olefin mer" refers to a unit in, for example, an ethylene/alpha-olefin copolymer, the polymerization unit being that "residue" which is derived from the alpha-olefin monomer after it reacts to become a portion of the polymer chain, i.e., that portion of the polymer contributed by an individual alpha-olefin monomer after it reacts to become a portion of the polymer chain.

As used herein, "EVOH" refers to ethylene vinyl alcohol copolymer. EVOH includes saponified or hydrolyzed ethylene vinyl acetate copolymers, and refers to a vinyl alcohol copolymer having an ethylene comonomer, and prepared by, for example, hydrolysis of vinyl acetate copolymers, or by chemical reactions with polyvinyl alcohol. The degree of hydrolysis is preferably from about 50 to 100 mole percent; more preferably, from about 85 to 100 mole percent.

As used herein, the phrases "vinyl polymer" and "vinyl resin" are used interchangeably, and refer to all resins and polymers made from monomers containing the vinyl group, $H_2C=CHX$, wherein X can be hydrogen, halogen, saturated or unsaturated hydrocarbon radical, acrylic-type ester, etc., and also includes polyvinylchloride, polyvinylidene chloride, ethylene/vinyl alcohol copolymer, ethylene/vinyl acetate copolymer, etc.. Preferred vinyl polymers include polyethylene homopolymer, ethylene/alpha-olefin copolymer, ethylene/ester copolymer (especially ethylene/vinyl acetate copolymer).

Preferably, the vinyl polymer comprises at least one member selected from the group consisting of ethylene mer, propylene mer, alpha-olefin mer, aromatic mer, anhydride mer, ester mer, acid mer, and amide mer. More preferably, the vinyl resin comprises at least one member selected from the group consisting of ethylene mer, alpha-olefin mer, aromatic mer, anhydride mer, ester mer, and acid mer; more preferably, at

least one member selected from the group consisting of ethylene mer and alpha-olefin mer.

The fatty amide is grafted to the vinyl polymer by reacting the fatty amide with unsaturated sites on the vinyl polymer. If the vinyl polymer has no unsaturated sites thereon, the vinyl polymer can be reacted with a peroxide, in order to form unsaturated sites which are reactive with the fatty amide, to result in a grafted fatty amide vinyl polymer. The temperature and pressure within an extruder is appropriate for carrying out both the reaction of the peroxide with the vinyl polymer, as well as for carrying out the reaction of the unsaturated sites of the vinyl polymer with the fatty amide.

As used herein, the phrase "heterogeneous polymer" refers to polymerization reaction products of relatively wide variation in molecular weight and relatively wide variation in composition distribution, i.e., polymers made, for example, using conventional Ziegler-Natta catalysts. Heterogeneous polymers are useful in various layers of the film used in the present invention. Such polymers typically contain a relatively wide variety of chain lengths and comonomer percentages.

As used herein, the phrase "heterogeneous catalyst" refers to a catalyst suitable for use in the polymerization of heterogeneous polymers, as defined above. Heterogeneous catalysts are comprised of several kinds of active sites which differ in Lewis acidity and steric environment. Ziegler-Natta catalysts are heterogeneous catalysts. Examples of Ziegler-Natta heterogeneous systems include metal halides activated by an organometallic co-catalyst, such as titanium chloride, optionally containing magnesium chloride, complexed to trialkyl aluminum and may be found in patents such as U.S. Patent No. 4,302,565, to GOEKE, et. al., and U.S. Patent No. 4,302,566, to KAROL, et. al., both of which are hereby incorporated, in their entireties, by reference thereto.

As used herein, the phrase "homogeneous polymer" refers to polymerization reaction products of relatively narrow molecular weight distribution and relatively narrow composition distribution. Homogeneous polymers can be used in various layers of multilayer films useful in the present invention. Homogeneous polymers are structurally different from heterogeneous polymers, in that homogeneous polymers exhibit a relatively even sequencing of comonomers within a chain, a mirroring of sequence distribution in all chains, and a similarity of length of all chains, i.e., a narrower molecular weight distribution. Furthermore, homogeneous polymers

are typically prepared using metallocene, or other single-site type catalysis, rather than using Ziegler Natta catalysts.

More particularly, homogeneous ethylene/alpha-olefin copolymers may be characterized by one or more methods known to those of skill in the art, such as molecular weight distribution (M_w/M_n), composition distribution breadth index (CDBI), narrow melting point range, and single melt point behavior. The molecular weight distribution (M_w/M_n), also known as "polydispersity," may be determined by gel permeation chromatography. Homogeneous ethylene/alpha-olefin copolymers which can be used in the present invention preferably have an M_w/M_n of less than 2.7; more preferably from about 1.9 to 2.5; still more preferably, from about 1.9 to 2.3. The composition distribution breadth index (CDBI) of such homogeneous ethylene/alpha-olefin copolymers will generally be greater than about 70 percent. The CDBI is defined as the weight percent of the copolymer molecules having a comonomer content within 50 percent (i.e., plus or minus 50%) of the median total molar comonomer content. The CDBI of linear polyethylene, which does not contain a comonomer, is defined to be 100%. The Composition Distribution Breadth Index (CDBI) is determined via the technique of Temperature Rising Elution Fractionation (TREF). CDBI determination clearly distinguishes homogeneous copolymers (i.e., narrow composition distribution as assessed by CDBI values generally above 70%) from VLDPEs available commercially which generally have a broad composition distribution as assessed by CDBI values generally less than 55%. TREF data and calculations therefrom for determination of CDBI of a copolymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation as described, for example, in Wild et. al., J. Poly. Sci. Poly. Phys. Ed., Vol. 20, p.441 (1982). Preferably, the homogeneous ethylene/alpha-olefin copolymers have a CDBI greater than about 70%, i.e., a CDBI of from about 70% to 99%. In general, the homogeneous ethylene/alpha-olefin copolymers useful in the present invention also exhibit a relatively narrow melting point range, in comparison with "heterogeneous copolymers", i.e., polymers having a CDBI of less than 55%. Preferably, the homogeneous ethylene/alpha-olefin copolymers exhibit an essentially singular melting point characteristic, with a peak melting point (T_m), as determined by Differential Scanning Colorimetry (DSC), of from about 60°C to 105°C. Preferably the homogeneous copolymer has a DSC peak T_m of from about 80°C to 100°C. As used herein, the phrase "essentially single melting point" means

that at least about 80%, by weight, of the material corresponds to a single T_m peak at a temperature within the range of from about 60°C to 105°C, and essentially no substantial fraction of the material has a peak melting point in excess of about 115°C., as determined by DSC analysis. DSC measurements are made on a Perkin Elmer System 7 Thermal Analysis System. Melting information reported are second melting data, i.e., the sample is heated at a programmed rate of 10°C./min. to a temperature below its critical range. The sample is then reheated (2nd melting) at a programmed rate of 10°C/min.

A homogeneous ethylene/alpha-olefin copolymer can, in general, be prepared by the copolymerization of ethylene and any one or more alpha-olefin. Preferably, the alpha-olefin is a C_3 - C_{20} alpha-monoolefin, more preferably, a C_4 - C_{12} alpha-monoolefin, still more preferably, a C_4 - C_8 alpha-monoolefin. Still more preferably, the alpha-olefin comprises at least one member selected from the group consisting of butene-1, hexene-1, and octene-1, i.e., 1-butene, 1-hexene, and 1-octene, respectively. Most preferably, the alpha-olefin comprises octene-1, and/or a blend of hexene-1 and butene-1.

Processes for preparing and using homogeneous polymers are disclosed in U.S. Patent No. 5,206,075, to HODGSON, Jr., U.S. Patent No. 5,241,031, to MEHTA, and PCT International Application WO 93/03093, each of which is hereby incorporated by reference thereto, in its entirety. Further details regarding the production and use of homogeneous ethylene/alpha-olefin copolymers are disclosed in PCT International Publication Number WO 90/03414, and PCT International Publication Number WO 93/03093, both of which designate Exxon Chemical Patents, Inc. as the Applicant, and both of which are hereby incorporated by reference thereto, in their respective entireties.

Still another species of homogeneous ethylene/alpha-olefin copolymers is disclosed in U.S. Patent No. 5,272,236, to LAI, et. al., and U.S. Patent No. 5,278,272, to LAI, et. al., both of which are hereby incorporated by reference thereto, in their respective entireties.

As used herein, the term "polyolefin" refers to any polymerized olefin, which can be linear, branched, cyclic, aliphatic, aromatic, substituted, or unsubstituted. More specifically, included in the term polyolefin are homopolymers of olefin, copolymers of olefin, copolymers of an olefin and an non-olefinic comonomer copolymerizable with the olefin, such as vinyl monomers, modified polymers thereof, and the like. Specific examples include polyethylene homopolymer, polypropylene homopolymer, polybutene, ethylene/alpha-olefin copolymer,

propylene/alpha-olefin copolymer, butene/alpha-olefin copolymer, ethylene/vinyl acetate copolymer, ethylene/ethyl acrylate copolymer, ethylene/butyl acrylate copolymer, ethylene/methyl acrylate copolymer, ethylene/acrylic acid copolymer, ethylene/methacrylic acid copolymer, modified polyolefin resin, ionomer resin, polymethylpentene, etc. Modified polyolefin resin is inclusive of modified polymer prepared by copolymerizing the homopolymer of the olefin or copolymer thereof with an unsaturated carboxylic acid, e.g., maleic acid, fumaric acid or the like, or a derivative thereof such as the anhydride, ester or metal salt or the like. It could also be obtained by incorporating into the olefin homopolymer or copolymer, an unsaturated carboxylic acid, e.g., maleic acid, fumaric acid or the like, or a derivative thereof such as the anhydride, ester or metal salt or the like.

As used herein, terms identifying polymers, such as "polyamide", "polyester", "polyurethane", etc. are inclusive of not only polymers comprising repeating units derived from monomers known to polymerize to form a polymer of the named type, but are also inclusive of comonomers, derivatives, etc. which can copolymerize with monomers known to polymerize to produce the named polymer. For example, the term "polyamide" encompasses both polymers comprising repeating units derived from monomers, such as caprolactam, which polymerize to form a polyamide, as well as copolymers derived from the copolymerization of caprolactam with a comonomer which when polymerized alone does not result in the formation of a polyamide. Furthermore, terms identifying polymers are also inclusive of "blends" of such polymers with other polymers of a different type.

As used herein, the phrase "anhydride functionality" refers to any form of anhydride functionality, such as the anhydride of maleic acid, fumaric acid, etc., whether blended with one or more polymers, grafted onto a polymer, or copolymerized with a polymer, and, in general, is also inclusive of derivatives of such functionalities, such as acids, esters, and metal salts derived therefrom.

As used herein, the phrase "modified polymer", as well as more specific phrases such as "modified ethylene vinyl acetate copolymer", and "modified polyolefin" refer to such polymers having an anhydride functionality, as defined immediately above, grafted thereon and/or copolymerized therewith and/or blended therewith. Preferably, such modified polymers have the anhydride functionality grafted on or polymerized therewith, as opposed to merely blended therewith.

As used herein, the phrase "anhydride-containing polymer" refers to one or more of the following: (1) polymers obtained by copolymerizing an anhydride-containing monomer with a second, different monomer, and (2) anhydride grafted copolymers, and (3) a mixture of a polymer and an anhydride-containing compound.

5 The term "ionomer", as used herein, refers to a product of an ionic polymerization, i.e., a polymer containing interchain ionic bonding. Preferably, the ionomer comprises at least one member selected from the group consisting of a thermoplastic resin based on metal salt of an alkene/acid copolymer; more preferably, a thermoplastic resin based on metal salt of ethylene/acid copolymer; still more preferably, metal salt of ethylene/methacrylic acid
10 copolymer. As used herein, the term "ionomer" also includes ethylene/acrylic acid copolymer and ethylene/acid/acrylate terpolymer.

As used herein, the phrases "ethylene alpha-olefin copolymer", and "ethylene/alpha-olefin copolymer", refer to such heterogeneous materials as low density polyethylene (LDPE), medium density polyethylene (MDPE), linear low density polyethylene (LLDPE), and very
15 low and ultra low density polyethylene (VLDPE and ULDPE); as well as to such homogeneous ethylene/alpha olefin copolymers as: metallocene-catalyzed EXACT (TM) linear homogeneous ethylene/alpha olefin copolymer resins obtainable from the Exxon Chemical Company, of Baytown, Texas, homogeneous substantially linear ethylene/alpha-olefin copolymers having long chain branching (e.g., copolymers known as AFFINITY (TM)
20 resins, and ENGAGE (TM) resins, available from the Dow Chemical Company, of Midland, Michigan), as well as TAFMER (TM) linear homogeneous ethylene/alpha-olefin copolymer resins obtainable from the Mitsui Petrochemical Corporation. Both the heterogeneous polymers and homogeneous polymers referred to above generally include copolymers of ethylene with one or more comonomers selected from C₄ to C₁₀ alpha-olefin such as butene-1
25 (i.e., 1-butene), hexene-1, octene-1, etc. While LDPE and MDPE are more highly branched than LLDPE, VLDPE, ULDPE, EXACT (TM) resin, and TAFMER (TM) resin, this latter group of resins has a relatively large number of short branches rather than the longer branches present in LDPE and MDPE. AFFINITY (TM) resins and ENGAGE (TM) resins have a relatively large number of short branches in combination with a relatively small number of
30 long-chain branches. LLDPE has a density usually in the range of from about 0.91 grams per cubic centimeter to about 0.94 grams per cubic centimeter.

In general, the ethylene/alpha-olefin copolymer comprises a copolymer resulting from the copolymerization of from about 80 to 99 weight percent ethylene and from 1 to 20 weight percent alpha-olefin. Preferably, the ethylene alpha-olefin copolymer comprises a copolymer resulting from the copolymerization of from about 85 to 95 weight percent ethylene and from
5 5 to 15 weight percent alpha-olefin.

As used herein, the phrases "inner layer" and "internal layer" refer to any layer, of a multilayer film, having both of its principal surfaces directly adhered to another layer of the film.

As used herein, the phrase "inside layer" refers to an outer film layer, of a multilayer
10 film packaging a product, which is closest to the product, relative to the other layers of the multilayer film. "Inside layer" also is used with reference to the innermost layer of a plurality of concentrically arranged layers simultaneously coextruded through an annular die.

As used herein, the phrase "outer layer" refers to any film layer of film having less than two of its principal surfaces directly adhered to another layer of the film. The phrase is
15 inclusive of monolayer and multilayer films. All multilayer films have two, and only two, outer layers, each of which has a principal surface adhered to only one other layer of the multilayer film. In monolayer films, there is only one layer, which, of course, is an outer layer in that neither of its two principal surfaces are adhered to another layer of the film.

As used herein, the phrase "outside layer" refers to the outer layer, of a multilayer film
20 packaging a product, which is furthest from the product relative to the other layers of the multilayer film. "Outside layer" also is used with reference to the outermost layer of a plurality of concentrically arranged layers simultaneously coextruded through an annular die.

As used herein, the phrase "directly adhered", as applied to film layers, is defined as adhesion of the subject film layer to the object film layer, without a tie layer, adhesive, or other
25 layer therebetween. In contrast, as used herein, the word "between", as applied to a film layer expressed as being between two other specified layers, includes both direct adherence of the subject layer between to the two other layers it is between, as well as including a lack of direct adherence to either or both of the two other layers the subject layer is between, i.e., one or more additional layers can be imposed between the subject layer and one or more of the layers
30 the subject layer is between.

As used herein, the term "core", and the phrase "core layer", as applied to multilayer films, refer to any inner film layer which has a primary function other than serving as an adhesive or compatibilizer for adhering two layers to one another. Usually, the core layer or layers provide the multilayer film with a desired level of strength, i.e., modulus, and/or optics, and/or added abuse resistance, and/or specific impermeability.

As used herein, the phrases "seal layer," "sealing layer," "heat seal layer," and "sealant layer," refer to an outer film layer, or layers, involved in the sealing of the film to itself, another film layer of the same or another film, and/or another article which is not a film. It should also be recognized that in general, up to the outer 3 mils of a film can be involved in the sealing of the film to itself or another layer. With respect to packages having only fin-type seals, as opposed to lap-type seals, the phrase "sealant layer" generally refers to the inside film layer of a package, as well as supporting layers within 3 mils of the inside surface of the sealant layer, the inside layer frequently also serving as a food contact layer in the packaging of foods. In general, sealant layers employed in the packaging art have included thermoplastic polymers, such as polyolefin, polyamide, polyester, and polyvinyl chloride.

As used herein, the phrase "tie layer" refers to any inner film layer having the primary purpose of adhering two layers to one another. Tie layers can comprise any polymer having a polar group thereon, or any other polymer which provides sufficient interlayer adhesion to adjacent layers comprising otherwise nonadhering polymers.

As used herein, the phrase "skin layer" refers to an outside layer of a multilayer film in packaging a product, this skin layer being subject to abuse.

As used herein, the phrase "bulk layer" refers to any layer of a film which is present for the purpose of increasing the abuse-resistance, toughness, modulus, etc., of a multilayer film. Bulk layers generally comprise polymers which are inexpensive relative to other polymers in the film which provide some specific purpose unrelated to abuse-resistance, modulus, etc.

The names "first layer", "second layer", as used herein, are generally indicative of the manner in which a multilayer film structure is built up. That is, in general, the first layer can be present without any of the additional layers described, or the first and second layers can be present without any of the additional layers described, etc.

As used herein, the term "extrusion" is used with reference to the process of forming continuous shapes by forcing a molten plastic material through a die, followed by cooling or

chemical hardening. Immediately prior to extrusion through the die, the relatively high-viscosity polymeric material is fed into a rotating screw of variable pitch, i.e., an extruder, which forces the polymeric material through the die.

As used herein, the term "coextrusion" refers to the process by which the outputs of
5 two or more extruders are brought smoothly together in a feed block, to form a multilayer stream that is fed to a die to produce a layered extrudate. Coextrusion can be employed in film blowing, sheet and flat film extrusion, blow molding, and extrusion coating.

As used herein, the phrase "machine direction", herein abbreviated "MD", refers to a direction "along the length" of the film, i.e., in the direction of the film as the film is formed
10 during extrusion and/or coating. As used herein, the phrase "transverse direction", herein abbreviated "TD", refers to a direction across the film, perpendicular to the machine or longitudinal direction.

As used herein, the phrase "free shrink" refers to the percent dimensional change in a 10 cm x 10 cm specimen of film, when shrunk at 185°F, with the quantitative determination
15 being carried out according to ASTM D 2732, as set forth in the 1990 Annual Book of ASTM Standards, Vol. 08.02, pp. 368-371, which is hereby incorporated, in its entirety, by reference thereto.

The multilayer films useful in the article and process of the present invention has at least 3 layers (preferably from 3 to 20 layers), and preferably has at least 4 layers (more
20 preferably from 4 to 12 layers; still more preferably, from 4 to 11 layers; and yet still more preferably, from 6 to 10 layers). However, so long as the multilayer film has at least 3 layers, the multilayer film can have any further number of additional layers desired, so long as the film provides the desired properties for the particular packaging operation in which the film is used, e.g. O₂-barrier characteristics, free shrink, shrink tension, optics, modulus, seal strength, etc.
25 The multilayer film illustrated in Figure 1 comprises five layers; in Figure 2, six layers; in Figure 3, six layers.

The multilayer film used in the present invention can have any total thickness desired, so long as the film provides the desired properties for the particular packaging operation in which the film is used. Preferably, the film has a total thickness of less than about 20 mils, more
30 preferably the film has a total thickness of from about 0.2 to 10 mils, still more preferably from about 0.3 to 5 mils, and yet still more preferably, from about 1.5 to 4 mils.

Optionally, the film of the present invention can be irradiated to induce crosslinking. In the irradiation process, the film is subjected to an energetic radiation treatment, such as corona discharge, plasma, flame, ultraviolet, X-ray, gamma ray, beta ray, and high energy electron treatment, which induce cross-linking between molecules of the irradiated material.

5 The irradiation of polymeric films is disclosed in U.S. Patent No. 4,064,296, to BORNSTEIN, et. al., which is hereby incorporated in its entirety, by reference thereto. BORNSTEIN, et. al. discloses the use of ionizing radiation for crosslinking the polymer present in the film.

To produce crosslinking, a suitable radiation dosage of high energy electrons, preferably using an electron accelerator, with a dosage level being determined by standard

10 dosimetry methods. Other accelerators such as a Van de Graaf generator or resonating transformer may be used. The radiation is not limited to electrons from an accelerator since any ionizing radiation may be used. The ionizing radiation can be used to crosslink the polymers in the film. Preferably, the film is irradiated at a level of from 2-15 MR (20-150 kGy), more preferably 2-10 MR (20-100 kGy). As can be seen from the descriptions of

15 preferred films for use in the present invention, the most preferred amount of radiation is dependent upon the film composition, thickness, etc., and its end use.

The film of the present invention is particularly useful in the production of bags for packaging fresh red meat, smoked and processed meat, pork, cheese, poultry, and the like, as described in e.g. U.S. Patent Nos. 3,741,253 (Brax et al.), 3,891,008

20 (D'Entremont), 4,048,428 (Baird), and 4,284,458 (Schirmer), each of which is hereby incorporated, in its entirety, by reference thereto. The film can be of a type suitable for use in bags used for cook-in applications, e.g., as disclosed in U.S. Patent No. 4,064,296, to Bornstein et al, entitled "HEAT SHRINKABLE MULTI-LAYER FILM OF

25 HYDROLYZED ETHYLENE VINYL ACETATE AND A CROSS-LINKED OLEFIN POLYMER", as well as U.S. Patent No. 4,855,183, to T.T. Oberle, entitled "MULTIPLE LAYER, COOK-IN FILM," each of which is hereby incorporated, in its entirety, by reference thereto.

For example, the film can be used as a shrink film in packaging applications for packaging food and non-food items. Films in which the present invention can be

30 beneficially used are described in, e.g., U.S. Patent Nos. 4,551,380 and 4,643,943, both to Schoenberg, both hereby incorporated, in their entirety, by reference thereto.

The present invention can also be used with films having oxygen, moisture, or odor barrier functionality, as described in, e.g., U.S. Patent No. 4,064,296, to Bornstein et al., U.S. Patent No. 4,724,185 to Shah, U.S. Patent No. 4,839,235 to Shah, and U.S. Patent No. 5,004,647 also to Shah, each of which is hereby incorporated in its entirety by
5 reference thereto.

The film of the present invention can also be used as or in connection with films used in patch bags, i.e., a patch bag as described in U.S. Patent No. 4,755,403, to Ferguson, hereby incorporated, in its entirety, by reference thereto.

The film can also be of a type suitable for use a medical film application, e.g., in
10 the film disclosed in U.S.S.N. 08/408,667, filed March 22, 1995, in the name of W. B. MUELLER, entitled "FILMS FOR MEDICAL SOLUTION POUCHES," the entirety of which hereby incorporated by reference thereto; as well as in U.S.S.N. 08/408,668, filed March 22, 1995, in the name of W.B. Mueller, entitled "MULTILAYER FILMS FOR PACKAGING AND ADMINISTERING MEDICAL SOLUTIONS," the entirety of
15 which is also hereby incorporated by reference thereto.

The film can also be of a type suitable for use in a thermoformed package, e.g., as disclosed in U.S. Patent No. 4,735,855, to Wofford et al., entitled "THERMOFORMABLE LAMINATE," the entirety of which is also hereby incorporated by reference thereto.

20 The film can also be of the stretch/shrink type, e.g., as disclosed in U.S. Patent No. 4,617,241, to W.B. Mueller, entitled "LINEAR POLYETHYLENE STRETCH/SHRINK FILM," the entirety of which is also hereby incorporated by reference thereto.

The film can also be of a type suitable for the packaging of high acid food
25 products, e.g., as disclosed in U.S. Patent No. 4,746,562, to E.M. Fant, entitled "PACKAGING FILM," the entirety of which is also hereby incorporated by reference thereto.

The film can also be of a type suitable for the packaging, water cooking, and storing food within the package, e.g., as disclosed in U.S. Patent No. 4,104,404, to Anne
30 C. Bieler et al., entitled "CROSS-LINKED AMIDE/OLEFIN POLYMERIC TUBULAR

FILM COEXTRUDED LAMINATES," the entirety of which is also hereby incorporated by reference thereto.

The film can also be a hot blown film of a type useful in chub packaging, e.g., as disclosed in U.S. Patent No. 4,937,112, to H.G. Schirmer, entitled "HIGH STRENGTH
5 COEXTRUDED FILM FOR CHUB PACKAGING," as well as U.S. Patent No. 4,909,726, to S. Bekele, entitled "IMPACT-RESISTANT FILM FOR CHUB PACKAGING," the entirety each of which is hereby incorporated by reference thereto.

The film can also be of a type having improved physical characteristics through the use of linear low density polyethylene or linear medium density polyethylene resin in a
10 core and/or an intermediate layer, e.g., as disclosed in U.S. Patent No. 4,532,189 to W.B. Mueller, entitled "LINEAR POLYETHYLENE SHRINK FILMS," U.S. Patent No. 4,194,039 to W.B. Mueller, entitled "MULTI-LAYER POLYOLEFIN SHRINK FILM," U.S. Patent No. 4,390,385 to D.J. Ferguson et al, entitled "HEAT-SEALABLE, MULTI-PLY POLYPROPYLENE FILM," U.S. Patent No. 4,274,900 to W.B. Mueller et al,
15 entitled "MULTI-LAYER POLYESTER/POLYOLEFIN SHRINK FILM," U.S. Patent No. 4,188,443 to W.B. Mueller et al, entitled "MULTI-LAYER POLYESTER/POLYOLEFIN SHRINK FILM," and, U.S. Patent No. 5,298,302 to P.R. Boice, entitled "FILM WITH IMPROVED LAP SEAL," each of which is hereby incorporated, in its entirety, by reference thereto.]

20 The film can also be a low shrink energy film, e.g., as disclosed in U.S. Patent No. 4,833,024, to W.B. Mueller, entitled "LOW SHRINK ENERGY FILMS," as well as U.S. Patent No. 5,023,143, to M. Nelson, entitled "LOW SHRINK FORCE SHRINK FILM," the entirety each of which is hereby incorporated by reference thereto.

The film can also be of a type suitable for use in vacuum skin packaging, e.g., as
25 disclosed in U.S. Patent No. 4,886,690, to K.A. Davis et al, entitled "PEELABLE BARRIER FILM FOR VACUUM SKIN PACKAGES AND THE LIKE," as well as U.S. Patent No. 4,963,427, to Botto et al, entitled "MULTILAYER PACKAGING FILM," U.S. Patent No. 5,075,143, to Bekele, entitled "HIGH BARRIER IMPLOSION RESISTANT FILMS," the entirety each of which is hereby incorporated by reference
30 thereto.

The film can also be of a type suitable for use in films comprising homogeneous polymer, e.g., as disclosed in U.S.S.N. 07/976,122, to R. Babrowicz et al, entitled "HEAT SHRINKABLE FILMS CONTAINING SINGLE SITE CATALYZED COPOLYMERS," U.S.S.N. 08/018,657, to K. Ahlgren et al., entitled "HEAT SHRINKABLE FILMS
5 CONTAINING SINGLE SITE CATALYZED COPOLYMERS HAVING LONG CHAIN BRANCHING," U.S.S.N. 08/124,179, to K. Ahlgren, entitled "HEAT SHRINKABLE FILMS CONTAINING SINGLE SITE CATALYZED COPOLYMERS," U.S.S.N. 08/418,926, to R. Babrowicz et al, entitled "HEAT SHRINKABLE FILMS CONTAINING SINGLE SITE CATALYZED COPOLYMERS," U.S.S.N. USSN
10 08/481,782, to R. Babrowicz et al, entitled "HIGH IMPACT STRENGTH FILM CONTAINING SINGLE SITE CATALYZED COPOLYMER," and, U.S. Patent No. 5,491,019 to Kuo, entitled "OXYGEN-PERMEABLE MULTILAYER FILM," the entirety each of which is hereby incorporated by reference thereto.

The film can be used as or in connection with irradiated, oriented, heat set films.
15 Additionally, the film of the invention can be laminated, adhesively adhered, extrusion coated, or extrusion laminated onto a substrate to form a laminate.

Example

Low density polyethylene (about 99.8 percent by weight) is mixed with both ethyl 3,3-Di(t-amylperoxy)butyrate (0.05 percent by weight) and erucamide (0.2 percent by weight) in a
20 twin screw extruder. In the extruder, the various components reach a temperature of about 360°F, for a time of from about 30 seconds to 5 minutes, during which the components are mixed to substantial homogeneity while being subjected to the high degree of shear imposed by the twin screw extruder. The erucamide is grafted onto the low density polyethylene and thereafter extruded through a die so that a monolayer film is formed. The resulting monolayer
25 film has a coefficient of friction of about 0.25 per ASTM D 1894, which is hereby incorporated in its entirety, by reference thereto.

Although the present invention has been described in connection with the preferred embodiments, it is to be understood that modifications and variations may be utilized without departing from the principles and scope of the invention, as those skilled in the art will readily
30 understand. Accordingly, such modifications may be practiced within the scope of the following claims.

WHAT IS CLAIMED IS:

1. A film having an outer layer comprising a vinyl polymer having grafted fatty amide thereon.

5

2. The film according to Claim 1, wherein the grafted fatty amide comprises at least one member selected from the group consisting of grafted erucamide, grafted oleamide, grafted linoleamide, and grafted linolenamide.

10

3. The film according to Claim 1, wherein the film is a multilayer film.

4. The film according to Claim 3, wherein the multilayer film and is biaxially-oriented and heat-shrinkable and comprises:

15

(A) a first layer, the first layer being an outer layer, the first layer comprising an ethylene/alpha-olefin copolymer having a major differential scanning calorimetry peak of less than 105°C;

(B) a second layer, the second layer being an inner O₂-barrier layer; and

20

(C) a third layer, the third layer being a second outer layer, the third layer comprising at least one member selected from the group consisting of ionomer, homogeneous ethylene/alpha-olefin copolymer, ethylene/acrylic acid copolymer, ethylene/methyl acrylic acid copolymer, ethylene/vinyl acetate copolymer, and propylene/ethylene copolymer having an ethylene content of at least 10 percent; and

wherein the multilayer film has a free shrink, at 185°F, of at least 80 percent, and all layers of the multilayer film are shrink-compatible with respect to one another.

25

5. The multilayer film according to Claim 3, comprising a first layer having been subjected to an energetic radiation surface treatment in a dosage of up to about 12 MR, said first layer comprising polyamide.

30

6. The multilayer film according to Claim 3, comprising:

(A) a first layer comprising a first homogeneous ethylene/alpha-olefin copolymer;

(B) a second layer comprising polyolefin; and

(C) a third layer comprising a second homogeneous ethylene/alpha-olefin copolymer;

and

wherein the second layer is between the first layer and the third layer, the second layer is
5 chemically different from the first layer and the third layer, and the multilayer film has an
oxygen transmission rate of from about 500 to 50,000 cc/m² 24hr STP.

7. The multilayer film according to Claim 3, comprising:

(A) a first outer layer comprising:

10 (i) a polymeric component comprising at least one member selected from the group
consisting of ethylene homopolymer, ethylene/alpha-olefin copolymer,
ethylene/ester copolymer, ethylene/acid copolymer, and ionomer; and

(ii) a surface-active agent component comprising at least one member selected from
the group consisting of ester of aliphatic alcohol, polyether, polyhydric alcohol,
15 ester of polyhydric aliphatic alcohol, and polyethoxylated aromatic alcohol;

(B) at least one inner layer comprising polyolefin; and

(C) a second outer layer comprising at least one member selected from the group
consisting of ethylene homopolymer, ethylene/alpha-olefin copolymer, ethylene/ester
copolymer, ethylene/acid copolymer, and ionomer;

20 wherein the surface-active component is present over the entire outside surface of the first
outer layer, the inner layer is between the first outer layer and the second outer layer, the
inner layer is chemically different from the first outer layer and the second outer layer, and
the multilayer film has an O₂-transmission rate of from about 500 to 50,000 cc/m² 24hr STP.

25 8. The multilayer film according to Claim 3, wherein the multilayer film is heat
shrinkable and comprises:

(A) first and second layers each of which is an outer layer; and

(B) a third layer which is an inner layer comprising from 70 to 90 weight percent,
based on layer weight, of at least one member selected from the group
30 consisting of ethylene homopolymer and ethylene copolymer, butylene
homopolymer, and butylene copolymer, wherein from about 10 to 30 weight

percent of the third layer is selected from the group consisting of butylene homopolymer and butylene copolymer; and
wherein at least one film layer comprises at least one member selected from the group consisting of propylene homopolymer and propylene copolymer.

5

9. The multilayer film according to Claim 3, comprising:

(A) a first layer consisting essentially of a crosslinked ethylene/vinyl acetate copolymer;

(B) a second layer comprising an O₂-barrier material comprising vinyl chloride-vinylidene chloride copolymer; and

(C) a third layer comprising a non-crosslinked ethylene/vinyl acetate copolymer.

10. The multilayer film according to Claim 3, comprising:

(A) an inner layer comprising homogeneous ethylene/alpha-olefin copolymer having a density of from about 0.89 to 0.92 grams per cubic centimeter;

(B) a first outer layer comprising at least one member selected from the group consisting of propylene homopolymer, propylene copolymer, a blend of homopolymer or copolymer of polypropylene and elastomer, high density polyethylene, and copolyester; and

(C) a second outer layer comprising at least one member selected from the group consisting of polyamide, copolyamide, polyester, copolyester, high density polyethylene, polypropylene, propylene/ethylene copolymer, and polycarbonate.

11. The multilayer film according to Claim 3, comprising:

(A) a first layer comprising a blend of elastomer and at least one member selected from the group consisting of propylene homopolymer and propylene copolymer; and

(B) a second layer in adherence with the first layer, the second layer comprising an ethylene/alpha-olefin copolymer having a density of less than or equal to 0.89 grams per cubic centimeter.

30

12. The multilayer film according to Claim 3, comprising:

- (A) a first layer and a second layer, both of which are outer layers containing a polymer comprising at least one member selected from the group consisting of: (i) olefin, and (ii) polyester; and
- (B) a third layer which is an inner layer and which comprises polyolefin; and
- 5 wherein the third layer is between the first layer and the second layer and the film has a maximum average machine direction shrink tension of no more than about 300 psi, and a maximum average transverse direction shrink tension of no more than about 300 psi, said shrink tension values being measured under ASTM D 2838, and the polymer in the first and second layers comprises polymer having a melting point at least about 10°C higher
- 10 than a melting point of the polyolefin in the third layer.

13. The multilayer film according to Claim 3, wherein the multilayer film comprises a gas permeable film which can be manually delaminated from a gas impermeable film, wherein:

- 15 (A) the gas-permeable film comprises:
- (i) a first layer which serves as a heat-sealable layer and which comprises at least one member selected from the group consisting of ethylene homopolymer and ethylene copolymer; and
- (ii) a second layer which comprises linear ethylene/alpha-olefin copolymer
- 20 having a density of less than about 0.915 g/cc; and
- (B) the gas-impermeable film comprises:
- (i) a first layer which comprises at least one member selected from the group consisting of ethylene/vinyl alcohol copolymer, vinylidene chloride copolymer, and vinylidene chloride terpolymer, this first layer
- 25 being directly to the second layer of the gas-permeable film in a manner so that when delamination occurs the barrier layer becomes a first surface layer; and
- (ii) a second layer comprising a polymer, the second layer being an outer layer; and

wherein the first layer of the gas-permeable film is capable of sealing to a polymeric surface with a bond strength greater than a force required to rupture and subsequently delaminate the gas-permeable film from the gas-impermeable film.

5 14. The multilayer film according to Claim 3, wherein the multilayer film is suitable for use in vacuum skin packaging, the multilayer film comprising:

- (A) a first layer which is a bonding layer comprising at least one member selected from the group consisting of low density polyethylene, high density polyethylene, and ionomer;
- 10 (B) a second layer which is a complementary layer comprising an ethylene/vinyl acetate copolymer comprising vinyl acetate mer in an amount of from about 15 to 25 percent, based on copolymer weight, the remainder of the copolymer comprising ethylene mer, wherein the copolymer is crosslinked, the second layer having a thickness of from about 16 to 225 microns; and
- 15 (C) a third layer which is an outer layer which is coextruded with the first layer, the second layer being between the first layer and the third layer, the third layer comprising at least one member selected from the group consisting of low density polyethylene, high density polyethylene, linear low density polyethylene, ionomer, and ethylene vinyl acetate copolymer having a vinyl
- 20 acetate content of from about 3 to 9 percent, based on copolymer weight.

15 15. A heat-shrinkable film comprising a homogeneous single-site catalyzed copolymer of ethylene and an alpha-olefin having from three to ten carbon atoms, said copolymer having a density of at least about 0.90 g/cc, wherein the film has an outer

25 surface comprising a vinyl polymer having grafted fatty amide thereon.

16. The multilayer film according to Claim 3, wherein the film is heat-shrinkable and has a substantially symmetrical structure comprising:

- (A) outer layers comprising at least one member selected from the group
- 30 consisting of propylene homopolymer and propylene copolymer; and

- (B) an inner layer comprising a homogeneous single-site-catalyzed copolymer of ethylene and an alpha-olefin having from four to eight carbon atoms.

5 17. The multilayer film according to Claim 3, wherein the film is heat-shrinkable and comprises:

- (A) a first layer which is an outer layer and which serves as a heat sealing layer;
- 10 (B) a second layer which is an inner layer and which comprises a homogeneous single-site-catalyzed copolymer of ethylene and an alpha-olefin having from three to ten carbon atoms, the copolymer having a density of at least about 0.90 g/cc; and
- (C) a third layer which is an O₂-barrier layer.

15 18. The multilayer film according to Claim 3, wherein the film is heat-shrinkable and comprises:

- (A) a first layer which is an outer layer and which serves as a heat sealing layer comprising a homogeneous single-site-catalyzed copolymer of ethylene and an alpha-olefin having from three to eight carbon atoms, the
- 20 copolymer having a density of at least about 0.90 g/cc; and
- (B) a second layer which is an O₂-barrier layer.

 19. The multilayer film according to Claim 3, wherein the film is heat-shrinkable and comprises at least one layer comprising a homogeneous single-site-catalyzed

25 copolymer of ethylene and an alpha-olefin having from three to eight carbon atoms, the copolymer having a density of at least about 0.90 g/cc, wherein at least one layer of the film comprises a crosslinked polymer network.

 20. The multilayer film according to Claim 3, wherein the film is heat-shrinkable

30 and has a substantially symmetrical structure comprising:

- (A) first and second outer layers comprising a homogeneous single-site-catalyzed copolymer of ethylene and an alpha-olefin having from three to eight carbon atoms, the copolymer having a density of at least about 0.90 g/cc,
- (B) a third layer which is an inner layer.

5

21. The film according to Claim 3, wherein the heat shrinkable film has an impact strength of at least 35 pounds, per mil of homogeneous polymer.

INTERNATIONAL SEARCH REPORT

Int. l. Application No.

PCT/US 97/13551

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08J5/18 B32B27/30 B32B27/16 C08L51/00

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08J C08F B32B C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	EP 0 791 628 A (MITSUI PETROCHEMICAL IND) 27 August 1997 see page 7, line 19-21-37 - page 13, line 27-39; claims 1,7,13,14 ---	1,3,15
P,X	EP 0 749 989 A (MITSUI PETROCHEMICAL IND) 27 December 1996 see page 17, line 43-51 - page 19, line 17-20; claims 1,3 ---	1,3,15
X	US 5 407 713 A (WILFONG DEBRA L ET AL) 18 April 1995 Y see column 7, line 34-50 - column 21, line 29-61; claims 1,2,6-9 ---	1,3 4,15
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

19 November 1997

Date of mailing of the international search report

12/12/1997

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Derz, T

INTERNATIONAL SEARCH REPORT

Int. l. Application No

PCT/US 97/13551

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 173 (M-1581), 24 March 1994 & JP 05 338102 A (SHOWA DENKO KK), 21 December 1993, see abstract ---	1,3
X	US 5 132 172 A (SIMPSON J THOMAS ET AL) 21 July 1992	1,3
A	see column 3, line 3-27 - column 4, line 3-14; claim 1 ---	5
X	US 4 460 632 A (ADUR ASHOK M ET AL) 17 July 1984	1,3
Y	see column 2, line 5-7 - column 4, line 15-39; claims 1,4,7,10,11,25,26	4
A	---	10
X	EP 0 534 015 A (GRACE W R & CO) 31 March 1993 see claims 1,12; example 5 ---	1,3
X	PATENT ABSTRACTS OF JAPAN vol. 095, no. 004, 31 May 1995 & JP 07 011068 A (SHOWA DENKO KK), 13 January 1995, see abstract ---	1
X	PATENT ABSTRACTS OF JAPAN vol. 095, no. 004, 31 May 1995 & JP 07 011069 A (SHOWA DENKO KK), 13 January 1995, see abstract ---	1
Y	PATENT ABSTRACTS OF JAPAN vol. 095, no. 011, 26 December 1995 & JP 07 195637 A (MITSUI PETROCHEM IND LTD), 1 August 1995, see abstract -----	15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/13551

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0791628 A	27-08-97	JP 9077923 A	25-03-97
		JP 9077924 A	25-03-97
		JP 9087603 A	31-03-97
		WO 9710297 A	20-03-97
EP 0749989 A	27-12-96	DE 69314137 D	30-10-97
		EP 0598628 A	25-05-94
		JP 6206939 A	26-07-94
		CA 2103379 A	20-05-94
		JP 6206922 A	26-07-94
		JP 6206924 A	26-07-94
		JP 6206923 A	26-07-94
US 5407713 A	18-04-95	US 5643375 A	01-07-97
		CA 2123809 A	24-06-93
		EP 0617665 A	05-10-94
		JP 7502219 T	09-03-95
		WO 9311938 A	24-06-93
		US 5496295 A	05-03-96
US 5132172 A	21-07-92	US 5308428 A	03-05-94
		AU 600278 B	09-08-90
		AU 7412087 A	17-12-87
		CA 1326626 A	01-02-94
		JP 63011339 A	18-01-88
		KR 9510586 B	20-09-95
US 4460632 A	17-07-84	US 4460745 A	17-07-84
		CA 1200043 A	28-01-86
		DE 3313607 A	03-11-83
		FR 2525622 A	28-10-83
		GB 2119389 A,B	16-11-83
		JP 58194967 A	14-11-83
		JP 62011038 B	10-03-87
		NL 8301280 A,B,	16-11-83
EP 0534015 A	31-03-93	JP 3285903 A	17-12-91